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## (54) OXYCARBONYLATION OF ETHYLENE OR PROPYLENE

(71) We, RÖHM G.M.B.H., a German Body Corporate, of Darmstadt, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and 5 the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a novel 10 process for the oxycarbonylation of ethylene or propylene, and is an improvement in or modification of the invention described and claimed in British Patent Specification No. 1,419,577.

It is known to prepare unsaturated carbonylic acids by the oxycarbonylation of olefins, i.e. the reaction of olefins with carbon monoxide and oxygen in an anhydrous medium under pressure and at elevated temperature. 15 In this reaction, a salt or a soluble complex 20 compound of a platinum metal catalyses the reaction. Among the platinum metals, palladium and/or a compound thereof have proved particularly effective catalysts. U.S. Patent Specification No. 3,381,030, for example describes a process for the oxycarbonylation of 25 olefins. Since water can be formed as a result of side-reactions thereby affecting the course of the main reaction, dehydrating agents may be used in the above-mentioned oxycarbonylation 30 reaction. Examples of such dehydrating agents include acid anhydrides and chlorides, and also ketene.

As described in U.S. Patent Specification 35 No. 3,621,054, molecular sieves based on aluminium silicates can be used as dehydrating agents; such macromolecular sieves can be prepared as described in U.S. Patent Specifications Nos. 2,882,243 and 2,882,244.

The catalytic activity of the platinum 40 metals and/or the salts of these metals can generally be considerably improved by using a Redox metal in conjunction with such catalyst. According to U.S. Patent Specification 3,397,226, copper has proved particularly suitable as a polyvalent metal which, together with 45 for example a palladium salt, can form a cata-

lytic Redox system. According to U.S. Patent Specification No. 3,415,871 iron salts can also be used for the same purpose.

The above mentioned U.S. Patent Specification No. 3,397,226 describes the oxycarbonylation of olefins in an anhydrous alcohol, and indicates that the esters of the resulting unsaturated carboxylic acids are accordingly produced. Don Fenton and Ken Olivier have reviewed in CHEMTECH, April 1972, pages 220 to 225, the oxycarbonylation of olefins in the presence of platinum metals as catalysts. As the result of an intensive 10-years study, Fenton and Olivier have proposed that the oxycarbonylation of olefins is performed most favourably in the presence of a Redox system made up of a palladium salt and a copper salt. The use of a catalytic system consisting partly of palladium salts has, however, disadvantages arising from the high price of this metal, the difficulty of separating the palladium from copper or other heavy metals, and the susceptibility of the catalytic system to catalyst poisons, in particular phosphorus, arsenic and sulphur.

In our British Patent Specification No. 1,419,577, we describe and claim a process for the preparation of  $\alpha,\beta$ -unsaturated carbonylic acids which comprises reacting oxygen and carbon monoxide with ethylene or propylene under substantially anhydrous conditions in a solvent medium, the reaction being carried out in the presence of a catalyst system comprising, or derived from:—

a) at least one solvent-soluble compound of aluminium or an alkaline earth metal (as hereinafter defined); and  
 b) at least one solvent-soluble compound of palladium or an element in group IV B, V B, VI B or VII B of the periodic system (as hereinafter defined) with the exception of rhenium.

We have now found that the above-described oxycarbonylation reaction, the subject of our said British Patent Specification, can be carried out with advantage by using a sol-

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vent-soluble compound of silicon, phosphorus, gallium or germanium in place of, or in addition to, component a) of the above-defined catalyst system, and/or a solvent-soluble compound of iron or copper in place of, or in addition to, component b) of the catalyst system.

According to the present invention therefore we provide a process for the oxycarbonylation of ethylene or propylene which comprises reacting oxygen and carbon monoxide with ethylene or propylene under substantially anhydrous conditions in a solvent medium, the reaction being carried out in the presence of a catalyst system comprising

A) at least one solvent-soluble compound of silicon, phosphorus, gallium or germanium; and at least one solvent-soluble compound of palladium or an element in group IV B, V B, VI B, or VII B of the periodic system (as hereinafter defined); or a complex derived from the said solvent-solvent compounds;

B) at least one solvent-soluble compound of aluminium or an alkaline earth metal (as hereinafter defined) and at least one solvent-soluble compound of iron or copper; or a complex derived from the said solvent-soluble compounds; or

C) at least one solvent-soluble compound of silicon, phosphorus, gallium or germanium and at least one solvent-soluble compound of iron or copper; or a complex derived from the said solvent-soluble compounds.

The references herein to an element in group IV B, V B, VI B or VII B of the periodic system (with the exception of rhenium) are intended to denote an element selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese or technetium. The term "alkaline earth metal" is used herein to denote an element selected from beryllium, magnesium, calcium, strontium or barium.

The above-defined catalyst system employed in accordance with the present invention may advantageously further contain one or more of the solvent-soluble catalytic compounds specified in our said British Patent Specification. Thus, catalyst system C) may, if desired, further contain a solvent-soluble compound of aluminium or an alkaline earth metal, and/or a solvent-soluble compound of palladium or of an element in group IV B, V B, VI B or VII B of the periodic system. Similarly, catalyst system A) may, if desired, further contain a solvent-soluble compound of aluminium or an alkaline earth metal while catalyst system B) may, if desired, further contain a solvent-soluble compound of palladium or of an element in group IV B, V B, VI B or VII B of the periodic system.

While it is not possible at present to give a fully satisfactory explanation of the mechanism of the catalytic reaction and of the functions ascribed to the components of the catalytic systems, it is believed that polynuclear complexes with catalytic metal ions are produced, wherein olefin molecules, carbonyl groups and oxygen are present as ligands. It has surprisingly been found that particularly active catalysts are those containing a cyanide or halide, in particular a chloride or bromide ion. If the above hypothesis concerning the formation of polynuclear complexes is correct, then the halide and cyanide ions could be present as ligands of the presumed complexes. In order to form such particularly active complexes, at least one of the metal compounds of the catalyst system can be used as a halide. Alternatively, the halide and/or cyanide of a further metal can be introduced into the reaction mixture forming the catalytic system. At the present time, it is not certain whether the advantages in reaction speeds and selectivity achieved when alkali metal carboxylates e.g. sodium or lithium acetate soluble in the reaction medium are also used, result merely from the buffer effect of the carboxylates in relation to the hydrochloric acid liberated from e.g. copper chloride or iron chloride during the reaction, or whether these carboxylates form particularly active complex-compounds with the above-mentioned metal compounds.

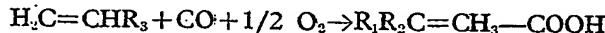
The catalytic systems employed according to the invention all promote the formation of  $\alpha$ - $\beta$ -unsaturated carboxylic acids by the oxycarbonylation of ethylene or propylene. It should however be emphasised that the selectivity of the various catalysts, particularly in regard to the oxycarbonylation of propylene, may be different. Whilst in the oxycarbonylation of ethylene, acrylic acid and (insofar as the reaction is performed in glacial acetic acid)  $\alpha$ - $\beta$ -acetoxypropionic acid are mainly formed, the corresponding reaction of propylene can lead to the two isomers, i.e. methacrylic acid and/or crotonic acid, and/or to the corresponding addition compounds of these acids with any carboxylic acid used as reaction medium. As is known,  $\beta$ -acetoxycarboxylic acid can easily be split into the corresponding  $\alpha$ - $\beta$ -unsaturated acid and glacial acetic acid. It should be pointed out that in the oxycarbonylation of olefins using the hitherto proposed processes, in addition to the formation of the desired  $\alpha$ - $\beta$ -unsaturated carboxylic acids, side reactions may take place resulting for example in the formation of glycol esters from olefins, oxygen, and the carboxylic acid serving as reaction medium, or in the formation of vinyl acetate from ethylene, oxygen and acetic acid. The new catalyst systems however generally have a good selectivity with regard to the formation of the unsaturated acids.

The reaction conditions employed for the process according to our said British Patent

Specification are generally applicable to the process according to the present invention. Thus the reaction is conveniently effected in a substantially anhydrous liquid solvent medium preferably at elevated temperature, i.e. at 20°C or more, advantageously at a

temperature between 80 and 200°C, although in individual cases it may be desirable to use higher temperatures up to e.g. 300°C. Even though the reactants namely olefin, CO and oxygen, can be used in stoichiometric amounts corresponding to the reaction equation

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15 wherein  $\text{R}_3$  is a hydrogen atom or a methyl group, in special cases it may be advantageous to use CO or also the olefin in excess. In order to avoid the formation of explosive mixtures, oxygen is preferably introduced continuously, advantageously at about the same rate as the oxygen is consumed in the reaction. The oxygen can be introduced not only in its pure form but also in the form of air.

20 The above reaction equation shows that the formation of the  $\alpha,\beta$ -unsaturated carboxylic acid is favoured by the use of pressure. The use of pressure alone is preferred for maintaining liquid phase conditions. Therefore even if the oxycarbonylation according to the invention can occur at normal pressure, the reaction is preferably carried out at elevated pressure, advantageously under a pressure of 1 to 200 atmospheres.

25 The process may be performed discontinuously or continuously.

30 Preferably the oxygen is introduced in such manner that the oxygen content of the outgoing gases is maintained below the explosive concentration, i.e. below about 10, preferably below about 3, vol. %. The excess gas, consisting mainly of olefin and carbon monoxide, can be recycled if desired back into the liquid reaction medium. The use of an inert gas, e.g. nitrogen, may be advantageous for avoiding explosive gas mixtures.

35 The amount of the catalyst used may vary within wide limits, depending upon the specific activity of the catalyst and upon the other reaction conditions. However, it may amount for example to 0.01 to 5% by weight of the liquid medium. From the above mentioned researches of Fenton and Olivier, it is known that the oxycarbonylation can be performed in an anhydrous medium and that water-binding agents can be added to the reaction medium to prevent undesired side reactions which might otherwise arise as a result of the formation of water during the reaction. Examples of such water-binding agents include the anhydrides and chlorides of carboxylic acids, e.g. the anhydride or chloride of a carboxylic acid serving as the liquid reaction medium. It is also possible to use molecular sieves based on aluminium silicates, for binding the water formed during the side reactions.

40 45 50 55 60 65 Preferably the reaction is carried out in an aliphatic carboxylic acid such as acetic acid or propionic acid, to which, as already indicated may be added, as water-binding agent, the anhydride or chloride of the particular acid

70 used. However other organic liquids, e.g. formamide, dimethylformamide, acetone, methyl-ethylketone, or cyclohexanone, may be used as reaction medium.

75 Particularly advantageous catalyst systems for use according to the invention, include those formed from a titanium compound and a phosphorus compound those formed from an aluminium and a copper compound, and those formed from a silicon and an iron-compound particularly for the oxycarbonylation of propylene to obtain methacrylic acid. The preparation of catalyst systems of this type is described in greater detail in the Examples. The silicon compound is preferably silicon tetrachloride; the phosphorus compound is preferably a chloride and/or oxychloride thereof; the compounds of gallium and germanium are preferably their halides. Iron and copper can be used for preparing the catalyst systems, e.g. in the form of their halides, sulphates, carboxylates, oxides, or complex salts, alone or in mixture with one another. The following Examples illustrate the present invention:—

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### Examples

In the following Examples, the process was carried out as follows:

The reaction medium comprising glacial acetic acid as solvent, acetic anhydride as water-binding agent, and the catalyst mixture, was placed in a Teflon-coated 2 litre autoclave fitted with a heater, the word "Teflon" is a registered Trade Mark. The autoclave was then closed. Propylene, on account of its low liquefying pressure, was compressed, to effect a saturation of the reaction medium. Afterwards, oxygen and carbon monoxide were added and the mixture was electrically heated to about 140—160°C. After a few hours reaction time it was cooled and the pressure released. The working up of the contents of the autoclave was effected by distillation.

The reaction products formed were analysed in conventional manner by gas chromatography, determination of the bromine number, and IR and NMR absorption spectra.

### Example 1

3 g of acetylacetone are dissolved in 25 ml of glacial acetic acid and reacted successively with 2.2 g of phosphorus pentachloride and 1.4 g of titanium tetrachloride. The precipitated crystals are suction filtered off and washed with a small amount of cold glacial

acetic acid. The titanium-phosphorus-complex thus formed is dissolved in 475 ml of glacial acetic acid and reacted with a further 25 ml of acetic anhydride. The reaction solution is placed in the high-pressure autoclave, and is saturated with propylene; afterwards it is provided with 80 atm. of carbon monoxide and 20 atm. oxygen, and electrically heated to about 150°C. At this temperature, the pressure slowly begins to fall. After cooling and release of pressure the mixture is worked up by distillation to yield:—

15      4.7 g 1,2-propanediol diacetate  
        0.4 g methacrylic acid  
        3.3 g crotonic acid  
        15.6 g  $\beta$ -acetoxy-n-butyric acid

Example 2  
20      2 g of copper-II-chloride and 2 g of aluminium acetate are dissolved in 490 ml of glacial acetic acid and 10 ml of acetic anhydride. After the saturation with propylene 20 atm. of oxygen and 80 atm. of carbon monoxide are compressed in and the mixture is heated to 153°C. At this temperature the pressure falls from 156 atm. to about 136 atm. Working up by distillation yields 3 g of propyleneglycol diacetate, 0.4 g of methacrylic acid, 4.8 g of crotonic acid, and 15.9 g of  $\beta$ -acetoxy-n-butyric acid.

30      Example 3.  
35      As in Example 1, a complex salt is prepared from acetylacetone, silicon tetrachloride, and iron-III-chloride, in glacial acetic acid. The entire reaction solution is dissolved in 450 ml of glacial acetic acid and 50 ml of acetic anhydride, and is treated, as in Example 2, with propylene, carbon monoxide, and oxygen. The reaction mixture is electronically heated to about 140°C. The pressure thereby falls from 161 atm. to 123 atm. After cooling and release of pressure the mixture is worked up by distillation to yield:—

45      0.5 g methacrylic acid  
        11.1 g crotonic acid  
        2.3 g  $\beta$ -acetoxy-n-butyric acid  
        8.5 g 1,2 propanediol diacetate.

Example 4  
50      3 g titanium-III-acetylacetone, 2 g of potassium bromide, and 5 g of gallium-III-chloride are dissolved in 450 ml glacial acetic acid and 50 ml of acetic anhydride. As in the previous examples, propylene, carbon monoxide and oxygen, are added and subsequently the mixture is electrically heated up to 165°C. 55      The pressure thereby drops from a maximum of 136 atm. to 104 atm. After cooling, the mixture is worked up by distillation to yield:—

0.7 g methacrylic acid  
9.4 g crotonic acid  
16.1 g  $\beta$ -acetoxy-n-butyric acid  
6.6 g 1,2-propanediol diacetate.

Example 5  
65      3 g manganese-II-chloride, 2 g iron-III-chloride, 4 g aluminium acetate and 3 g of silicon tetrachloride are dissolved in 500 ml glacial acetic acid and 15 ml of acetic anhydride. As was described in Example 1, after the saturation of the catalyst solution with propylene, 20 atm. of oxygen and 80 atm. of carbon monoxide are compressed into the autoclave, and heating to 160°C is carried out. At this temperature a distinct decrease in the initial pressure is observed. After cooling and release of pressure, the contents of the autoclave are worked up by distillation and are analysed in the manner indicated. There were found:

70      9.8 g crotonic acid  
        2.0 g  $\beta$ -acetoxy-n-butyric acid  
        1.1 g methacrylic acid  
        12.3 g 1,2-propanediol diacetate.

#### WHAT WE CLAIM IS:—

85      1. A process for the oxycarbonylation of ethylene or propylene which comprises reacting oxygen and carbon monoxide with ethylene or propylene under substantially anhydrous conditions in a solvent medium, the reaction being carried out in the presence of a catalyst system comprising  
90      A) at least one solvent-soluble compound of silicon, phosphorus, gallium or germanium; and at least one solvent-soluble compound of palladium or an element in group IV B, V B, VI B, or VII B of the periodic system (as hereinbefore defined); or a complex derived from the said solvent-soluble compounds;  
95      B) at least one solvent-soluble compound of aluminium or an alkaline earth metal (as hereinbefore defined) and at least one solvent-soluble compound of iron or copper; or a complex derived from the said solvent-soluble compounds; or  
100      C) at least one solvent-soluble compound of silicon, phosphorus, gallium or germanium and at least one solvent-soluble compound of iron or copper; or a complex derived from the said solvent-soluble compounds.

105      2. A process as claimed in claim 1 wherein catalyst system A) further contains at least one solvent-soluble compound of aluminium or an alkaline earth metal.

110      3. A process as claimed in claim 1 wherein catalyst system B) further contains at least one solvent-soluble compound of palladium or of an element in group IV B, V B, VI B or VII B of the periodic system.

115      4. A process as claimed in claim 1 wherein catalyst system C) further contains at least

one solvent-soluble compound of aluminium or an alkaline earth metal and/or at least one solvent-soluble compound of a palladium or of an element in group IV B, V B, VI B or VII B of the periodic system. 5. A process as claimed in claim 1 wherein the said reaction is carried out in the presence of a catalyst system A) comprising at least solvent-soluble compound of phosphorus and at least one solvent-soluble compound of titanium, or a complex derived from the said compounds. 6. A process as claimed in claim 1 wherein the said reaction is carried out in the presence of a catalyst system B) comprising at least solvent-soluble compound of aluminium and at least one solvent-soluble compound of copper, or a complex derived from the said compounds. 7. A process as claimed in claim 1 wherein the said reaction is carried out in the presence of a catalyst system B) comprising at least solvent-soluble compound of silicon and at least one solvent-soluble compound of iron, or a complex derived from the said compounds. 8. A process as claimed in any of the preceding claims wherein at least one of the said solvent-soluble compounds of the catalyst system is in the form of a halide. 9. A process as claimed in any of the preceding claims wherein the catalyst system further contains one or more halides and/or cyanides of metals other than those specified in claim 1. 10. A process as claimed in any of the preceding claims wherein the said solvent-soluble compound of silicon comprises silicon tetrachloride. 11. A process as claimed in any of the preceding claims wherein the said solvent-soluble compound of phosphorus comprises a phosphorus chloride or phosphorus oxychloride. 12. A process as claimed in any of the preceding claims wherein the said solvent-soluble compound of iron or copper comprises an iron or copper halide, sulphate, carboxylate, oxide or complex salt. 13. A process as claimed in any of the preceding claims wherein the said solvent medium comprises an aliphatic carboxylic acid. 14. A process as claimed in any of the preceding claims wherein the reaction is carried out in the presence of a water-binding agent. 15. A process as claimed in claim 11 wherein the said water-binding agent comprises an aliphatic carboxylic acid chloride or anhydride. 16. A process as claimed in claims 13 and 15 wherein the said chloride or anhydride is the chloride or anhydride of the carboxylic acid comprising the solvent medium. 17. A process as claimed in any of the preceding claims wherein the reaction is carried out at a temperature of 20°C to 300°C. 18. A process as claimed in claim 17 wherein the reaction is carried out at a temperature of 80°C to 200°C. 19. A process as claimed in any of the preceding claims wherein the reaction is carried out under superatmospheric pressure. 20. A process as claimed in any of the preceding claims wherein the reaction is carried out under a pressure of up to 200 atmospheres. 21. A process as claimed in any of the preceding claims wherein the catalyst system is employed in an amount of 0.01 to 5% by weight of the solvent medium. 22. A process as claimed in claim 1 substantially as herein described. 23. A process for the oxycarbonylation of propylene substantially as herein described in the Examples. 24.  $\alpha,\beta$ -Unsaturated carboxylic acids whenever prepared by a process as claimed in any of the preceding claims.

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